



Dynamics Simulation of Vapour Assisted Ammonia Pollution Removal By Pulse Discharge Method

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Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 30-11-2014

Accepted: 19-1-2015

Key Words:

Ammonia

Removal efficiency

Vapour additive

Pulse discharge method

ABSTRACT

Though ammonia (NH_3) is one of the most highly produced inorganic chemicals in the world, its pollution disadvantage on air and water have drawn much attention. In this article, the NH_3 removal is investigated through pulse discharge method. A zero dimensional molecular reaction model is established and solved. The vapour assisting effect on the NH_3 gas removal is discussed due to the extremely soluble character of NH_3 . Simulation indicates that the vapour additive has affected the H_2 and N_2 generating process. For vapour with several thousand'th ratio mixed, the electron collision on H_2O has been ignored. The results show that lower concentration vapour improves the removal efficiency in a very small extent, but higher vapour deteriorates it, with the optimal mixing concentration ratio between H_2O and NH_3 as 0.75:1000. For vapour with several tenth ratio mixed, the electron collision process on H_2O molecules is considered. More H_2O additive has significantly improved the NH_3 removal efficiency by accelerating the H_2 and N_2 generation process. At the vapour ratio of 750%, the removal efficiency is 64.28%, which is remarkably higher than that of 37.81% without vapour added. H_2O additive has saving of 70% energy consumption. The initial NH_3 concentration is another factor to influence the removal efficiency. The higher the initial NH_3 input, the less the H_2O is decomposed into OH and H by electron impact, and the removal efficiency is decreased consequently.

INTRODUCTION

Ammonia, with the molecular structure of NH_3 , can be generated from many sources, such as the natural decay of organic substances, the artificially dry distillation of nitrogenous wastes, or the modern Haber-Bosch process reacted between nitrogen and hydrogen gases. As one of the most highly produced inorganic chemicals, ammonia (NH_3) is consumed in very large quantities in factories as essential reactant for synthesizing nitric acid, fertilizers, pharmaceuticals or even antimicrobial agents for food products (Ceresana 2012). In spite of its importance in production, the environmental pollution disadvantage of NH_3 has drawn much attention. Reports have shown that the upper respiratory tract of human being can be irritated by ammonia moisture in the air (Camargo & Alonso 2006). Due to its extremely soluble character, the NH_3 waste can easily pollute water. This has drawn worldwide emphasis on eutrophication and toxic problems of ammonia in water (Francis et al. 2005, Zhang et al. 2012). A necessary task for water protection is the nitrogen waste disposal including NH_3 . Moussavi et al. (2011) have found that both autotrophic and heterotrophic bacteria are effective in nitrogen removal through the nitrification/denitrification (SND) process in a bench-scale biotrickling filter. Such biofiltration for ammonia removal has attached importance in recent years (Pagans et al. 2005).

The adsorption by zeolite can further improve the NH_3 removal efficiency (Ashrafizadeh et al. 2008). Catalyst technique is another method for NH_3 removal (Huang et al. 2000, Hung 2013). For example, the TiO_2 can effectively decompose NH_3 through photocatalysis process (Shavisi et al. 2014).

When it comes to the pulse discharge technique, it dissociates the NH_3 molecules by electron collision. There are further mechanical reactions between NH_3 and its fragments, which are dissociated from NH_3 after electron collision (Xia et al. 2008). The pulse discharge technique has the benefits of low-cost and high efficiency. There have been thorough investigations on gas removal of hydrogen sulfide (H_2S), oxysulphide (SO_2), nitrogen oxides (N_xO_y) by discharge plasma technique (Lee et al. 2013, Beckers et al. 2013, Bai et al. 2012). But the NH_3 removal by such technique is leanly investigated. In this article, a zero dimensional reaction model is established and the water vapour assisting effect on NH_3 removal is focused on.

MATERIALS AND METHODS

To generate discharge, the electrons are injected from one electrode and thrust to another electrode in the reactor. The collision between electron and NH_3 occurs during the process. Due to the high thermal movement activities of the

species, the temperature of the discharged plasma is set at 5000 K. The electron concentration is set as 10^{14} cm^{-3} . The NH_3 gas pressure is 1 atm, which means that the NH_3 concentration is $2.457 \times 10^{19} \text{ cm}^{-3}$. The pulse discharge is restricted in rectangular form lasting for 5 ms. The total simulation period is selected as 20 ms in this study, and the final concentration at 20 ms of all the products is taken into consideration to evaluate the NH_3 removal effect.

Electron collision has decomposed NH_3 into NH_2 and H , which is active to participate in further reactions with NH_3 and other species such as N , H_2 , N_2 as well as NH . The kinetic reaction is decided by the reactant concentrations and reaction rate coefficients, and can be numerically formulated as

$$\frac{dn_i}{dt} = -\sum_{i,j} k_{ij} n_i n_j + \sum_{p,q} k_{pq} n_p n_q \quad \dots(1)$$

The time-resolved concentration variance of i^{th} species is derived from the losing process caused by the reaction between i^{th} and j^{th} species and the generating process caused by the reaction between p^{th} and q^{th} species. Every reaction in Eq. (1) is ruled by the rate coefficients of k_{ij} and k_{pq} , which can be present based on Arrhenius equation (Stepanov et al. 1993) as :

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad \dots(2)$$

Where, A is the Arrhenius constant of the given reaction, and E_a is the reaction activation energy. For the electron colliding and decomposing reaction of NH_3 , its rate coefficient is calculated from the Boltzmann equation of its collision cross sections as:

$$k = \left(\frac{2}{m_e}\right)^{1/2} \int_0^\infty E^{1/2} \sigma(E_e) f(E_e) dE_e \quad \dots(3)$$

Where, E_e and m_e are the electron energy and mass. $f(E_e)$ is the electron distribution function, and $\sigma(E_e)$ is the corresponding collision cross section (Behringer & Fantz 1994). For other reactions, the rate coefficients can be acquired from NIST database (NIST 2013).

Since, the NH_3 is extremely soluble in water, the H_2O assisting effect must be considered. The reaction model is depicted in Table 1. The time-resolved concentration evolutions of all species are obtained according to Equation 1 through Runge-Kutta algorithm. Such algorithm is solved by Matlab.

It should be noticed that there has no spatial terms in Equation 1. It means that the concentration distributions of all the species are uniformly hypothesized. A zero-dimensional reaction model has been established in this study,

Table 1: Main reactions and rate coefficients of NH_3 and H_2O through pulse discharge.

R.	Reaction paths	k / cm^3s^{-1}
1	$e^* + \text{NH}_3 \rightarrow \text{NH}_2 + \text{H} + e$	5.39×10^{-11}
2	$\text{NH}_3 + \text{H} \cdot \rightarrow \text{H}_2 + \text{NH}_2$	3.45×10^{-12}
3	$\text{NH}_2 + \text{H} \cdot \rightarrow \text{H}_2 + \text{NH}$	1.00×10^{-11}
4	$\text{NH} + \text{H} \cdot \rightarrow \text{H}_2 + \text{N}$	1.69×10^{-11}
5	$\text{NH} + \text{N} \rightarrow \text{N}_2 + \text{H} \cdot$	8.18×10^{-11}
6	$\text{NH} + \text{NH} \rightarrow \text{NH}_2 + \text{N}$	1.80×10^{-11}
7	$\text{NH} + \text{NH} \rightarrow \text{N}_2 + \text{H} \cdot + \text{H} \cdot$	1.16×10^{-19}
8	$\text{NH}_2 + \text{NH}_2 \rightarrow \text{NH}_3 + \text{NH}$	1.38×10^{-11}
9	$\text{NH}_3 + \text{NH} \rightarrow \text{NH}_2 + \text{NH}_2$	1.87×10^{-13}
10	$\text{NH}_2 + \text{H}_2 \rightarrow \text{NH}_3 + \text{H} \cdot$	2.39×10^{-12}
11	$\text{NH} + \text{H}_2 \rightarrow \text{H} \cdot + \text{NH}_2$	1.55×10^{-13}
12	$\text{NH}_2 + \text{N} \rightarrow \text{NH} + \text{NH}$	4.47×10^{-14}
13	$\text{NH}_2 + \text{H} \cdot \rightarrow \text{NH}_3$	3.01×10^{-30}
14	$\text{H}_2\text{O} + \text{NH}_2 \rightarrow \cdot\text{OH} + \text{NH}_3$	6.62×10^{-13}
15	$\text{H}_2\text{O} + \text{NH} \rightarrow \cdot\text{OH} + \text{NH}_2$	2.50×10^{-12}
16	$\text{H}_2\text{O} + \text{H} \cdot \rightarrow \cdot\text{OH} + \text{H}_2$	4.20×10^{-12}
17	$\text{H}_2\text{O} + \text{N} \rightarrow \cdot\text{OH} + \text{NH}$	1.55×10^{-12}
18	$\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}_2\text{O} + \text{H} \cdot$	6.09×10^{-16}
19	$\cdot\text{OH} + \text{NH}_3 \rightarrow \text{H}_2\text{O} + \text{NH}_2$	4.48×10^{-13}
20	$\cdot\text{OH} + \text{NH}_2 \rightarrow \text{H}_2\text{O} + \text{NH}$	2.65×10^{-11}
21	$\cdot\text{OH} + \text{NH} \rightarrow \text{H}_2\text{O} + \text{N}$	4.93×10^{-11}

and can obtain concentration evolution of every species in time scale.

RESULTS AND DISCUSSION

Effect of vapour additive at low concentration on NH_3 removal efficiency: Since NH_3 is usually mixed with vapour, the H_2O additive effect on NH_3 removal efficiency is discussed. In this part, the H_2O is at thousand'th concentration ratio to NH_3 , and the electron collision on H_2O molecules has been ignored. According to Table 1, H_2O can directly react with NH_2 , and transform the latter into OH radical and NH_3 . It also can react with NH , H , N or even H_2O . The generated OH radicals then participate in further reactions with NH_3 , NH_2 and NH . H_2O additive can effectively influence the NH_3 removal process, as shown in Fig. 1.

The initial H_2O concentration is ranged from 0 to $1.2375 \times 10^{17} \text{ cm}^{-3}$, with the concentration ratio to NH_3 as 0 to 5%. At lower concentration of H_2O , the removal efficiency has increased as shown in Fig. 1a. The optimal condition is at the concentration ratio between H_2O and NH_3 as 0.75%. At such a ratio, about 37.844% NH_3 molecules have

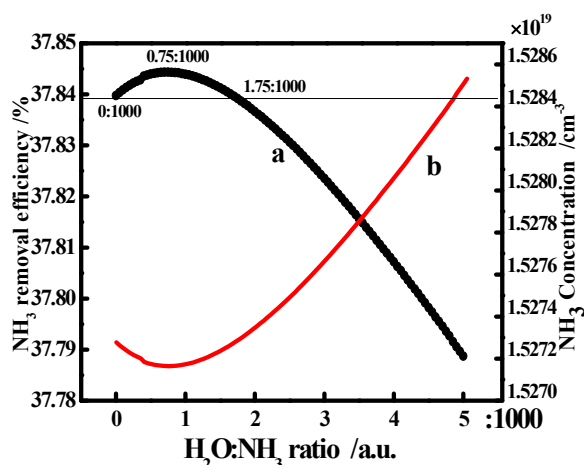


Fig. 1: (a) NH_3 removal efficiency, and (b) final NH_3 concentration under different concentration ratio of H_2O and NH_3 .

been removed, and is higher than 37.839% without H_2O added. This means that $1.1318 \times 10^{15} \text{ cm}^{-3}$ more NH_3 molecules have been removed.

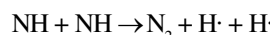
With H_2O concentration higher than 0.75%, the NH_3 removal efficiency decreases, and even becomes smaller than that without H_2O added when concentration ratio is higher than 1.75%. H_2O vapour has improved the removal process at lower additive concentration in a very small extent, but deteriorated the process at higher concentration.

Such a phenomenon is ascribed to the different varying trend of the produced species which are transformed from NH_3 , assisted by H_2O and its OH by-product.

More H_2O additive has affected the concentration of NH_2 and NH through the Reaction 14, 15, 20 and 21, and attenuated their further participation in the H_2 generation reac-

tions. As a result, the final H_2 concentration has decreased monotonically in Fig. 2a, and the final NH_2 and NH are kept with higher concentration left, when more H_2O is added (Fig. 2b). There are also more H elements finally reserved in Fig. 2b, which is not only due to the attenuated H_2 generating reactions, but also slightly affected by the H decomposed from H_2O in Reaction 18.

It is interesting that there appears maximal N_2 concentration in Fig. 2a when H_2O concentration increases. The N_2 molecule is generated from two paths between NH and N as



From the reaction model in Table 1, N elements can be consumed by H_2O in Reaction 17. More H_2O additive has obviously accelerated the consumption of N, and decreased its final concentration in Fig. 2b. Due to the contrary varying trends for the final concentration of NH and N , the maximal concentration of N_2 has reasonably appeared at the H_2O ratio of 1.35%.

According to the law of matter conservation, the removed NH_3 gas has transformed into N elements in N_2 , NH_2 , NH as well as N species, and H elements in H_2 , NH_2 , NH and H species. Based on the different varying trends in Fig. 2, the NH_3 removal efficiency has an optimal H_2O additive ratio of 0.75%, as shown in Fig. 1a. For vapour with thousand'th ratio mixed, less H_2O additive has improved the NH_3 removal efficiency in a very small extent.

Effect of vapour additive at high concentration on NH_3 removal efficiency: When vapour is mixed at tenth ratio of the NH_3 concentration, the electron collision reaction of H_2O molecules cannot be ignored. The dissociative thresh-

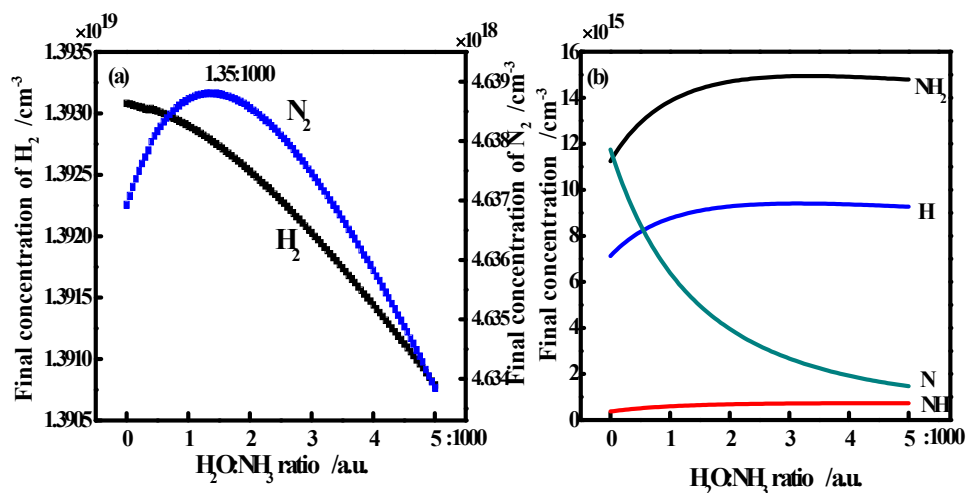


Fig. 2: (a) N_2 and H_2 final concentration, and (b) NH_2 , NH , N , H final concentration under different mixing ratios of H_2O and NH_3 .

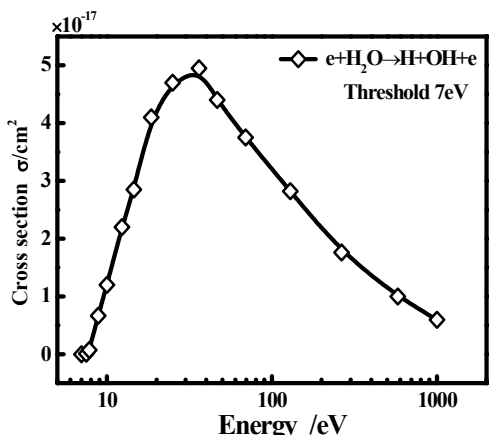
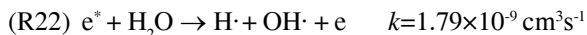


Fig. 3: Dissociative cross section of H₂O versus collision energy.

old of H₂O is 7eV, and its electron collision cross section is presented in Fig. 3.

By solving the Boltzmann Equation as ‘Eq. 3’, the rate coefficient is calculated as:



There are H and OH radicals generated. Since, the H radicals can participate in H₂ generation process, and the OH can react with NH₃, NH₂ and NH as ruled by Table 1, more effective removal is anticipated.

The final concentration of the NH₃ and its correspond removal efficiency is present in Fig. 4. The first decreasing, then increasing trend appears for removal efficiency. When vapour ratio is above 140%, the removal efficiency is achieved higher than that without vapour added. The H₂O additive at thousand'th concentration ratio has deteriorated the removal process, which has been discussed in

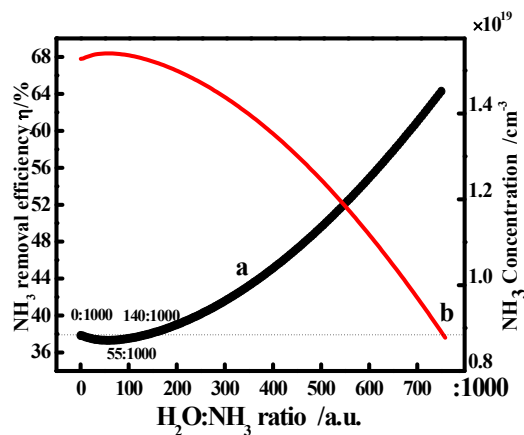


Fig. 4: (a) NH₃ removal efficiency, and (b) final NH₃ concentration under different concentration ratios of H₂O and NH₃.

the previous part. When the H₂O additive ratio is above 140%, the higher the H₂O concentration ratio is, the more effective the NH₃ removal efficiency becomes. At vapour ratio of 750%, the removal efficiency has been 64.285%, which is 26.441% higher than that of 37.844% removal efficiency without vapour added. Since the injected electron concentration is unchanged, the H₂O additive has saved energy consumption of about 70%.

A question should be answered, whether the major productions are benign. It is observed that H₂ and N₂ are the major ingredients transformed from NH₃, due to their higher concentration of 10¹⁹cm⁻³ and 10¹⁸cm⁻³ (Fig. 5a). Especially, the generated H₂ gas has decided the NH₃ removal efficiency. With vapour ratio increased to 750%, the H₂ concentration has accumulated to 2.398×10¹⁹cm⁻³, which is about 72.5% higher than 1.39×10¹⁹cm⁻³ of H₂ concentration without H₂O added. Consequently, the NH₃ removal efficiency has been

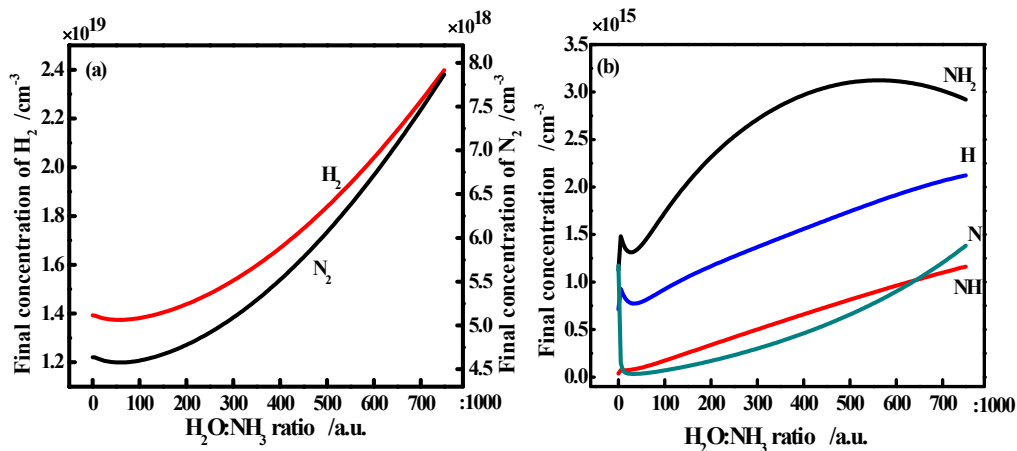


Fig. 5: (a) N₂ and H₂ final concentration, and (b) NH₂, NH, N, H final concentration under different mixing ratios of H₂O and NH₃.

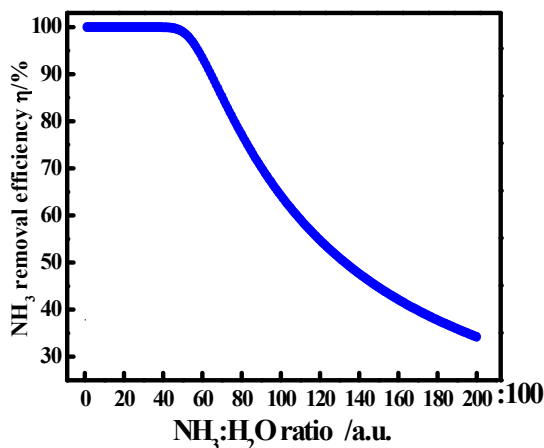


Fig. 6: NH_3 removal efficiency under different concentration ratios of NH_3 and H_2O .

significantly increased.

In Fig. 5b, the final concentrations of H and N at all vapour mixed ratios are lower than $1.74 \times 10^{15} \text{cm}^{-3}$, and the final NH_2 and NH concentration has been accumulated to 3.1×10^{15} and $8.1 \times 10^{14} \text{cm}^{-3}$. The NH_2 , NH , H as well as N are the minor or even have ignorable contribution to NH_3 removal.

For vapour with tenth ratio mixed, more H_2O additive has improved the NH_3 removal efficiency. Even improvement of 70% has been achieved at the vapour ratio of 750‰. The H and OH decomposed from H_2O by electron collision have played important role in the improvement.

Effect of initial NH_3 concentration on NH_3 removal efficiency: The initial concentration of NH_3 is another important factor affecting the removal effectiveness. With the initial concentration of NH_3 increased, the removal efficiency presents a monotonic decreasing trend in Fig. 6. There has been an abrupt change in the concentration ratio of 50% between NH_3 and H_2O . Below the point, the removal efficiency is slightly decreased from 100% and above the point, even more faster decrease has appeared. The higher the ratio is, the lower the removal efficiency becomes.

Such a trend is ascribed to the reason that the electron collision on H_2O is the major reaction when NH_3 concentration is relatively low, and the H and OH concentration is enough to remediate the NH_3 . Contrarily, the electron collision on NH_3 cannot be ignored when NH_3 concentration is increased, which means that the H and OH concentration has decreased due to the decreased electron collision probability on H_2O . The effect of H and OH on NH_3 removal ruled by Table 1 has subsequently weakened. The higher the NH_3 ratio is, the less the H and OH are generated from

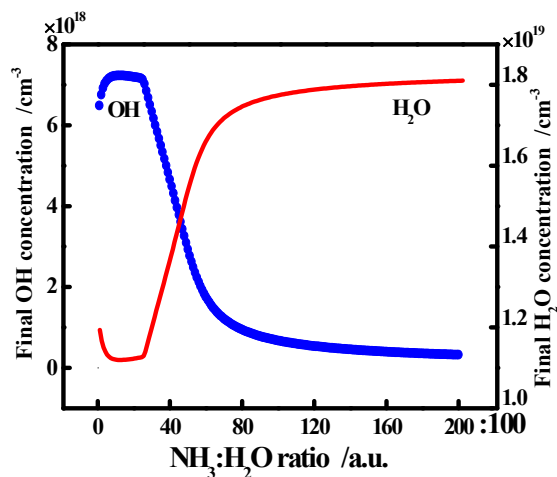


Fig. 7: OH and H_2O final concentration under different mixing ratios of NH_3 and H_2O .

H_2O by electron collision and participated in the NH_3 removal process.

The concentration evolution of OH in Fig. 7 has verified such variance. The higher the NH_3 concentration is, the less the OH radicals are finally preserved and more H_2O are left without participation in removal reactions to achieve assisting contributions.

CONCLUSIONS

Ammonia (NH_3) pollution in air and water has drawn much attention. The pulse discharge process for NH_3 remediation is simulated in this study. After establishing a zero dimensional reaction model, the vapour additive is observed as an effective method to influence the NH_3 removal efficiency by affecting the H_2 and N_2 generating process.

For vapour with thousand'th concentration ratio to NH_3 mixed, the electron decomposition of H_2O is ignored. Less H_2O additive has improved the NH_3 removal efficiency in a very small extent, but more additive deteriorates the removal process due to H_2O attenuating the production of H_2 and N_2 . The optimal mixing concentration ratio between H_2O and NH_3 is 0.75:1000.

For vapour with tenth ratio mixed, the electron collision on H_2O has been included. More H_2O additive has significantly improved the NH_3 removal efficiency by accelerating the H_2 and N_2 generation process. The H and OH decomposed from H_2O have played the important roles. Even 70% improvement has been achieved at the vapour ratio of 750‰ than that without H_2O additive.

Initial input of NH_3 concentration is another factor to influence the removal efficiency. The higher the NH_3 concentration is, the more the H_2O is left without decomposed

into H and OH for participation in the NH_3 removal reactions. The removal efficiency is consequently decreased.

ACKNOWLEDGMENTS

This work is financially supported by National Nature Science Foundation of China No. 10875036 and the Fundamental Research Funds for the Central Universities No. 12MS146.

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